The University of Alberta
Printing Department
Edmonton, Alberta

THE UNIVERSITY OF ALBERTA

HYDROLYSIS OF COORDINATED BENZONITRILES AND ELECTRON TRANSFER REACTIONS OF CARBOXAMIDO COMPLEXES OF PENTAAMMINECOBALT(III)

by

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A THESIS

SUBMITTED TO THE FACULTY OF

GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

Fall, 1973

TO MY PARENTS

ABSTRACT

The alkaline hydrolysis reactions of benzonitrile and 4-formylbenzonitrile complexes of pentaammine-cobalt(III) have been studied. The rate of the reaction was found to be first order with respect to hydroxide ion and the products of the reaction were the respective carboxamido complexes. The alkaline hydrolysis of the coordinated nitrile complexes seems to provide a general method for producing N-bonded carboxamido complexes.

The acid dissociation constant of the N isomer of benzamidopentaamminecobalt(III) has been determined. A general acid strengthening effect has been found upon coordination of carboxamido ligands to the $(NH_3)_5Co^{3+}$ moiety.

The chromium(II) reduction of the benzamido and 4-formylbenzamido cobalt(III) complexes were also studied. The rates of reduction of both reactions were first order with respect to the chromium(II) concentration and inversely dependent on the hydrogen ion concentration. The product analysis data indicate that the reduction of the benzamido cobalt(III) complex proceeds by two pathways: a major simple outer-sphere path and an inner-sphere path comprising ~11% of the overall reaction. A

comparison of the reduction of the 4-formylbenzamido cobalt(III) complex with the benzamido complex indicated that the former is also proceeding by a simple outer-sphere path. Since the rates for the two reactions are similar and the ligand reducibilities differ, it was concluded that a radical ion mechanism is not operating for the outer-sphere path. The minor path for the benzamido complex was regarded as proceeding by inner-sphere adjacent attack.

Acknowledgements

I wish to express my sincere gratitude to Dr. Robert B. Jordan for advice and guidance during this work. His thoughtfulness and understanding are inestimateable.

I also wish to thank Mrs. L. Ziola for the excellent preparation of this manuscript.

Financial assistance from the University of Alberta from 1970-1973 is gratefully acknowledged.

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CHAPTER I

INTRODUCTION

This study grew out of interest in the mechanisms of electron-transfer reactions between two metal centers, and is specifically concerned with a subclass of these reactions in which there is a change of one unit in oxidation state for the oxidizing agent and reducing agent. These are sometimes referred to as complementary electron transfer or oxidation-reduction reactions. Examples of two are given by equations I-1 and I-2.

$$Co(NH_3)_6^{3+} + Cr(OH_2)_6^{2+} + 6H^+ \rightarrow Co^{2+} + Cr(OH_2)_6^{3+} + 6NH_4^+ \qquad (I\text{-}1)$$

$$Co(NH_3)_5Cl^{2+} + Cr(OH_2)_6^{2+} + 5H^+ \rightarrow Co^{2+} + Cr(OH_5)Cl^{2+} + 5NH_4^+ \qquad (I\text{-}2)$$

These examples have been chosen to illustrate the two general mechanisms proposed for these reactions. In the case of reaction I-1, electron transfer takes place by an outer-sphere mechanism in which there is no interpenetration of coordination spheres of the two metal centers. On the other hand, reaction I-2

proceeds by an inner-sphere reaction mechanism in which a ligand is bonded to both the reductant and the oxidant in the activated complex. The chloride ligand in reaction I-2 is thus referred to as a bridging group. The simplest and most definitive confirmation of an inner-sphere mechanism is afforded by an analysis of the initial products to determine if the bridging group has been transferred from the oxidant to the reductant (as in I-2) or *vice versa*. In order to take advantage of this method of confirmation at least one of the reactants and one of the products must be sufficiently stable to permit separation and identification of the product. The cobalt(III)-chromium(II) electron transfer reaction has been widely studied since Co^{3+} and Cr^{3+} are substitution-inert and Co^{2+} and Cr^{2+} are substitution-labile. This is important because the analysis of the initial Cr(III) product, whether it is $(H_2O)_5CrL$ or $(H_2O)_6Cr$, can be taken to indicate an inner-sphere or outer-sphere mechanism respectively, as long as an initial chromium(III) complex does not undergo a fast reaction to produce $Cr(OH_2)_6^{3+}$. This possibility is minimized by the general inertness of chromium(III) complexes.

Outer-sphere reactions will occur when electron

transfer takes place more rapidly than does substitution into the coordination sphere of either reacting partner. It is recognized that an outer-sphere mechanism operates when both reactants are relatively inert to substitution, in addition, however, outer-sphere mechanisms may operate when one reaction partner is substitution labile. In reaction I-1 the coordinated NH_3 group does not have any unshared electrons to coordinate to the reductant Cr^{2+}. Therefore formation of an inner-sphere bridge with a normal coordinate bond is not possible.

The intimate mechanisms of inner-sphere electron transfer reactions have been discussed[1] and classified into four main mechanisms which are (1) double exchange — the reductant gives up the electron to the bridging group as the latter loses an electron to the oxidant; (2) superexchange — the bridging group provides vacant orbitals which serve to accept and transmit the reducing electron to the oxidant; (3) radical ion mechanism (chemical exchange) — the bridge is temporarily reduced before reduction of the oxidant; and (4) direct exchange — the bridging group serves only to bring the reactants together. Evidence supporting the four basic mechanisms has been presented in various systems.[2,3,4] These have

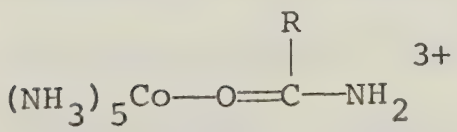
been classified[5] into two more general categories, the "chemical" and "resonance" mechanisms. The definition of "resonance" mechanism includes the superexchange and direct exchange previously proposed. In the "resonance" mechanism the electron is assumed to pass directly from the reducing agent to the oxidizing metal ion without occupying a bound state on the bridging ligand. On the other hand, the "chemical" mechanism (radical ion mechanism) refers to a process in which the reducing agent is strong enough to reduce the bridging ligand. That is, the electron passes from a bound state on the reducing agent to a bound state on the ligand before reaching the oxidizing center.

Nordmeyer and Taube[4] proposed that a "chemical" or radical ion mechanism is operating for the chromium(III) reduction of the nicotinamide ($3\text{-}NH_2C(O)C_5H_4N$) and isonicotinamide ($4\text{-}NH_2C(O)C_5H_4N$) pyridine bonded complexes of pentaamminecobalt(III). It was found in this study that the reduction of free isonicotinamide by Cr^{2+} is at least 50 times faster than the reduction of free nicotinamide under the same conditions. The specific rates for the inner-sphere reduction of isonicotinamidopentaamminecobalt-(III) is 500 times greater than that of the

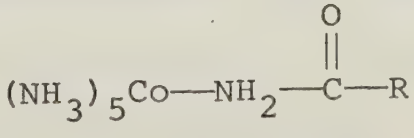
nicotinamidopentaamminecobalt(III). It was proposed[4] that the difference in the rates could be a reflection of the difference in the reducibilities of the ligands if both complexes are being reduced by an inner-sphere radical ion mechanism.

It has been proposed[6] recently that not only an inner-sphere radical ion mechanism but also an outer-sphere radical ion mechanism, where the coordination spheres of the two metal ion centers remain intact, is possible. The outer-sphere radical ion mechanism is expected to show a dependence on the reducibility of the ligand as did the inner-sphere mechanism. This is supported[6] by a linear free energy relationship between the log of the rate of reduction of some substituted benzonitrile ligands coordinated to pentaamminecobalt(III) and the Hammett σ^- constants of the substituents.

The observation[1] that the conjugate base of the N-isomer of the formamide complex is reduced much more rapidly than its parent acid (2) provided a hint to its electron transfer path.



(1)



(2)

The greater rate of reduction of the conjugate base may be associated with the ability of the nitrogen to π-bond with the C=O system. This may facilitate electron transfer to the cobalt(III), or it may provide a more stable radical ion intermediate, in which the electron is delocalized in the formamide π-antibonding system. As a result of the slow rate of reduction of the parent acid as compared to the reduction of the conjugate base, it was suggested that electron transfer should not occur readily through an $-NH_2$ group. This may be because two non-sigma bonding pairs of electrons are required for a bridging group.[1] One pair would be used in bonding to the reducing agent, and the other is in conjugation with the rest of the ligand system.

With two points in mind, the possibility of the radical ion mechanism operating and the conjecture that a protonated carboxamide breaks the conjugation between the aromatic ring and the oxidant, the following study was of special interest. The study of the N-bonded carboxamides perhaps could allow the detection of a radical ion intermediate. The electron may pass from the Cr^{2+} metal ion center by an inner-sphere remote attack or by an outer-sphere mechanism to the bridging ligand. If the $-NH_2$ group slows

down the passage of the electron to the Co(III) center, for reasons given above, then the electron may spend enough time on the ligand to provide a detectable intermediate.

It is appropriate at this point in our discussion to summarize the information required for a complete understanding of the mechanism of chromium(II) reduction of carboxamidopentaamminecobalt(III) complexes. It is most important to determine whether a ligand transfer product is formed. If ligand transfer occurs then an inner-sphere mechanism is operative. Once this has been established the detailed mechanism of the reaction must be elucidated. This involves determining the point of attack of the reductant on the ligand, obtaining a complete kinetic study of the reduction, and taking into account the stability of the initial products. Rate comparisons for different reductants and oxidants may be used to infer electronic pathways as was done for the nicotinamide example discussed above. In the present work the benzamide complexes with -H and 4-CHO substituents have been studied. Based on normal substituent effects the latter should be much more reducible and might favor some type of chemical or radical ion mechanism.

The coordination chemistry of the carboxamide

has shown that this group is normally oxygen bonded to transition metal ions.[7,8] Strong evidence has been given that under strong acid conditions carbonyl oxygen protonation occurs for amides and their N-methyl and N,N-dimethyl derivatives.[9,10] However, recent work has supported N-protonation for amides in dilute aqueous acid.[11,12] Reactions described in this work may provide a general method for preparing the unusual nitrogen bonded carboxamide complexes at least of $(NH_3)_5Co^{3+}$. The preparation of carboxamidopentaamminecobalt(III) complexes especially in the nitrogen bonded form would provide a further example of linkage isomerism (1),(2); and also further the understanding of the coordination chemistry of the carboxamide group.

In previous work[1] both the nitrogen and oxygen bonded isomers of formamide were obtained by reacting formamide with aquopentaamminecobalt(III). However, this does not appear to be a general method of preparation of N-bonded amide complexes since the O-bonded form seems to be generally favoured. The alkaline hydrolysis reactions (I-3) of nitrile bonded benzonitrile

$$(NH_3)Co{-}N{\equiv}C{-}R^{3+} + OH^- \rightarrow (NH_3)_5Co{-}\overset{H}{\underset{|}{N}}{-}\overset{O}{\underset{\|}{C}}{-}R \qquad (I\text{-}3)$$

and 4-formylbenzonitrile complexes of pentaammine-cobalt(III) have been studied and described in this thesis and seem to provide a general method for the preparation of N-bonded carboxamides. The products of the above reactions are the corresponding benzamido complexes bonded through the nitrogen atom as will be shown in the following chapters. Normally the hydrolysis of nitriles requires vigorous conditions.[13] However, it has been noted that the rate of alkaline hydrolysis of nitriles to the corresponding carboxamides is greatly enhanced by the presence of transition metal ions. For example, Breslow *et al*[14] found that the hydrolysis rate of 2-cyano-1,10-phenanthroline was increased by 10^7 in the presence of nickel(II). Recently, Bennett and Yoshida[15] have reported that tertiary phosphine hydroxy complexes of platinum(II) catalyze the hydrolysis of aliphatic nitriles under neutral conditions. In the present work the kinetics of hydrolysis of benzonitrile and 4-formylbenzonitrile coordinated to pentaamminecobalt(III) have been studied. This presents an extension of earlier work on similar systems.[1,6]

CHAPTER II

EXPERIMENTAL

(i) Preparation of Reagents

All solutions were prepared with water re-distilled from alkaline permanganate in an all glass apparatus. The sodium hydroxide solutions were prepared from ampoules of concentrated carbonate free reagent (J. T. Baker Chemical Co.). Lithium perchlorate solutions were prepared by dissolving a weighed sample of reagent grade lithium perchlorate (G. F. Smith Chemical Co.) in water. The resultant solution was filtered through a 5 micron Millipore filter (Millipore Filter Corp.) and standardized by passing an aliquot through a column of Dowex 50W - X8 cation exchange resin and determining the amount of hydrogen ion released. Perchloric acid solutions were prepared by dilution of 62% perchloric acid (J. T. Baker Chemical Co.) and standardized against sodium hydroxide.

Chromous perchlorate solutions were prepared by dissolving chromium metal (99.999% purity, United Mineral and Chemical Corp.) in a dilute perchloric acid/lithium perchlorate solution under high purity

argon (Union Carbide Ltd.) atmosphere. The total chromium content of these solutions was determined by oxidizing an aliquot of the chromous perchlorate solution to chromate, with an excess of 30% hydrogen peroxide in a sodium hydroxide solution. The excess hydrogen peroxide was destroyed by boiling the solution. The chromate was analyzed spectrophotometrically at 372 nm, and the chromium concentration was calculated from the known molar extinction coefficient (ε, 4.815×10^3 $M^{-1}cm^{-1}$) of chromate ion at this wavelength. The chromium(II) content of the chromous perchlorate solutions was determined by reacting an aliquot with an excess of standardized ferric ammonium sulfate solution under an argon atmosphere. The excess ferric ion was determined by addition of potassium iodide and titration of the liberated iodine with a standard sodium thiosulfate solution. Sodium thiosulfate solutions were prepared by dilution of ampoules of concentrated reagent (Bio-Rad Laboratories).

Vanadous perchlorate solution was prepared from vanadyl sulfate (A. D. Mackay, Inc.) by reduction with amalgamated zinc in a dilute perchloric acid/lithium perchlorate solution under an atmosphere of high purity argon. The vanadium(II) content of

the vanadous perchlorate solutions was not determined, as a result the rates of reduction of the complexes by V(II) are only approximate values. The main benefit of using V(II) for reduction was to determine the molar extinction coefficient of the ligand 4-formylbenzamide, thus only an approximately known strength of V(II) was required. It was assumed that the concentration of V(II) would closely approximate the value calculated from the known weight of vanadyl sulfate.

Solutions for chromium(II) and vanadium(II) reductions were de-oxygenated by purging with high purity argon and the reagents added by standard syringe techniques.

All other materials were used as supplied without further purification.

(ii) Preparation and Characterization of Complexes

1. Carbonatopentaamminecobalt(III) nitrate, $[(NH_3)_5CoCO_3][NO_3]$, and Aquopentaammine-cobalt(III) perchlorate, $[(NH_3)_5CoOH_2][ClO_4]_3$.

A solution of 225 gm of powdered ammonium carbonate in 225 ml of water and 325 ml of concentrated ammonium hydroxide was added to a solution of

150 gm of cobaltous nitrate in 75 ml of water and 50 ml of concentrated ammonium hydroxide. Upon stirring, the solution turned a deep crimson. The resulting mixture was air oxidized for a 24 hour period and cooled in a refrigerator for a further 24 hours. The bright red crystals were collected by filtration and washed thoroughly with methanol and ether and air-dried.

The carbonato complex was converted to aquopentaamminecobalt(III) perchlorate by slowly adding the red crystals to 400 ml of warm 1.0 M perchloric acid. The solution was cooled and the crystals collected by filtration. The aquo compound was recrystallized from 1.0 M perchloric acid to remove all traces of nitrate. The aquopentaamminecobalt(III) perchlorate was characterized by C, H, N analysis, by its pmr spectrum in deuterated dimethyl sulfoxide and by its visible absorption spectrum.
Anal. Calcd. for $[(NH_3)_5CoOH_2][ClO_4]_3$: N, 15.2; H, 3.69. Found:N, 15.10; H, 3.71.

It has been found that the chemical shift difference between the *cis* and *trans* NH_3 protons is 1.0 - 1.5 τ for an O-bonded ligand and 0 - 0.6 τ for an N-bonded ligand.[1] The results in Table 1 conform to this empirical rule. The relative shifts

of the *cis* and *trans* NH_3 protons have been discussed in a more theoretical manner by Hendrickson and Jolly.[16] The assignment of the *cis* and *trans* NH_3 protons is in accordance with integrated intensities and with previous work.[17]

2. Benzonitrile Complex, $[(NH_3)_5CoNCC_6H_5][ClO_4]_3$.

Aquopentaamminecobalt(III) perchlorate (5 gm) was dissolved in 50 ml of trimethylphosphate with 20 gm of Linde 3A molecular sieves and 5 gm of benzonitrile was then added. This mixture was heated on a steam bath at 70 - 80°C until the solution turned yellow-brown (1 - 2 hr). The molecular sieve was removed by filtration and the cooled filtrate treated with secondary butyl alcohol (800 ml) to precipitate the crude product. The precipitate was recrystallized by dissolving it in a minimum amount of warm water ($\leq$ 40°C) and adding sodium perchlorate until a saturated solution was produced. The solution was cooled and the resulting recrystallized product was collected by filtration, washed with ethanol, methanol and ether, and finally air dried.

Anal. Calcd. for $[(NH_3)_5CoNCC_6H_5][ClO_4]_3$: C, 15.4; N, 15.4; H, 3.66. Found: C, 15.32; N, 15.05; H, 3.71.

Table 1

Proton Magnetic Resonance Chemical Shifts for Pentaamminecobalt(III) Complexes in DMSO-d_6 [a]

Complex	*trans* NH_3	*cis* NH_3	Others
$[(NH_3)_5CoOH_2][ClO_4]_3$	7.20	6.21	OH_2, 4.33
$[(NH_3)_5CoNCC_6H_5][ClO_4]_3$	6.47	6.06	C_6H_5, 1.94, 2.05, 2.18, 2.21
$[(NH_3)_5CoNHCOC_6H_5][ClO_4]_2$ [b]	6.77	6.63	C_6H_5, 2.20, 2.53
$[(NH_3)_5CoNH_2COC_6H_5][ClO_4]_3$ [b,c,d]	6.72	6.58	C_6H_5, 2.27, 2.62
$[(NH_3)_5CoNCC_6H_4CHO][ClO_4]_3$	6.51	6.12	C_6H_4, 1.77 CHO, -0.14
$[(NH_3)_5CoNHCOC_6H_4CHO][I]_2$ [b]	(6.53)[e]	6.53	C_6H_4, 1.96 CHO, -0.14
$[(NH_3)_5CoNH_2COC_6H_4CHO][I]_3$ [b,c]	(6.48)[e]	6.48	C_6H_4, 1.98 CHO, -0.08

(a) All τ values are relative to the solvent peak at τ 7.48.

(b) The -NH and $-NH_2$ peaks of the ligand could not be definitely assigned.

(c) Produced by adding trifluoroacetic acid to a DMSO-d_6 solution of the unprotonated complex.

(d) This form rearranges to the O-bonded isomer in DMSO over a period of ~ 24 hr at room temperature.

(e) Peak not resolved but indicated to be under that of the *cis* NH_3 protons by integration.

The benzonitrile complex was characterized by microanalysis and visible, ultraviolet, infrared and proton magnetic resonance spectroscopy. The chemical shift difference between the *cis* and *trans* NH_3 protons indicates a nitrogen bonded ligand according to the empirical rule noted in the preceeding section.

The electronic spectrum of the benzonitrile complex is summarized in Table 2. The visible absorption spectrum is similar to $Co(NH_3)_6^{3+}$ (λ_{max} at 339 nm and 476 nm). The absorptions in the ultraviolet region are due to the nitrile ligand and to nitrile-cobalt(III) charge transfer bands since they are not observed in the hexaamminecobalt(III) complex.

The infrared spectrum of the benzonitrile complex shows the characteristic vibrations of coordinated NH_3 in the 3000, 1600, 1315, and 830 cm^{-1} regions.[18] The stretching frequency of the coordinated C≡N is 2270 cm^{-1}, an increase of 40 cm^{-1} relative to that of the free benzonitrile. This shift seems typical of cobalt(III) nitrile complexes.[1,6] An increased stretching frequency of the coordinated C≡N is also found for many pentaammineruthenium(III) nitrile complexes.[19] To account for this increase Purcell and Drago[20]

concluded, through calculations made on the force constants of some methyl cyanide adducts, that there must be an increasing C≡N force constant upon coordination. Purcell[21] further stated that all nitriles coordinated to Lewis acids show this increasing force constant due to a strengthening of the σ bonding between carbon and nitrogen. According to Purcell and Drago[20] a minor increase in frequency may be contributed by the coupling of the C≡N and M-N stretching vibrations. Metal d-electron back-bonding into the nitrile π* orbitals should decrease the C≡N stretching frequency, but this effect is overweighed by the factors discussed above.

3. The Conjugate Base of the N-isomer of Benzamidopentaamminecobalt(III), $[(NH_3)_5CoNHCOC_6H_5]^{2+}$

The N-bonded benzamido complex was prepared from the benzonitrile complex by dissolving the latter in a minimum amount of water and adding 5 M sodium hydroxide dropwise to a final pH of ~12. The solution was neutralized and subjected to ion exchange chromatography on Rexyn 102(H) (Fisher Scientific Co.) weak acid cation exchange

Table 2

Electronic Spectra of Pentaamminecobalt(III) Complexes[a]

Ligand	Absorption Maximum nm (Extinction Coefficient, $M^{-1}cm^{-1}$)		
Benzonitrile	469(79)	330(82)	233(2.2×10^4)[b]
$NHCOC_6H_5^-$	485(88.3)	345(117)	235(1.57×10^4)
$NH_2COC_6H_5$[c]	477(77.6)	342(89.5)	d
4-Formylbenzonitrile	472(77.5)		253(1.97×10^4)
$4\text{-}NHCOC_6H_4CHO^-$	484(91.5)		256(1.94×10^4) 220(2.95×10^4)
$4\text{-}NH_2COC_6H_4CHO$[c]	479(78.7)		256(1.97×10^4) 220(2.88×10^4)

(a) All spectra are in aqueous solution unless otherwise noted.

(b) A shoulder is also observed at ~270 nm (2.6×10^3).

(c) Obtained by adding unprotonated amide complex to ~1.0 M $HClO_4$.

(d) The untraviolet region of the spectrum was not recorded.

resin in the sodium ion form. The complex was eluted down the ion exchange column with sodium chloride solutions of increasing concentrations from 0.1 M. This procedure gave a separation into two bands with 0.3 M NaCl solution, an orange band separated and moved down the column leaving a red band at the top. The orange band of resin was separated physically and was washed with water and methanol, and then air dried. Since the product can be easily removed from the weak acid resin with a strong acid, the resin was then placed in a sintered glass filter and washed with 2 M perchloric acid. The filtrate was collected and neutralized by dropwise addition of 5 M NaOH. The resulting solution was saturated with sodium perchlorate, cooled and collected. However, analytical results always indicated that the product is a mixture of $[(NH_3)_5CoNHCOC_6H_5][ClO_4]_2$ and $[(NH_3)_5CoNH_2COC_6H_5][ClO_4]_3$.

As a result the unprotonated iodide salt was isolated by the following procedure. The perchlorate salt of the benzonitrile complex was dissolved in a minimum amount of water made basic by addition of sodium hydroxide. The pH of the solution was adjusted to a value of ~9. An excess of sodium iodide was added and the solution was cooled for

1 - 2 hr. The unprotonated iodide salt was recrystallized from alkaline solution by addition of sodium iodide. It should be noted that the iodide salt shows evidence of iodine if stored at room temperature for several weeks, but has been stored in a refrigerator for several months with no evidence of decomposition.

Anal. Calcd. for $[(NH_3)_5CoNHCOC_6H_5][I]_2 \cdot 2H_2O$: C, 15.16; N, 15.16; H, 4.51. Found: C, 15.43; N, 15.37; H, 4.51.

Because of difficulties encountered in preparing the perchlorate salt and possible oxidation of the iodide, the chloride salt was used in the determination of the acid dissociation constant of the carboxamido complex. The chloride salt was prepared by treating an aqueous solution of the perchlorate with tetraphenylarsonium chloride, then removing the tetraphenylarsonium perchlorate by filtration. The solution was acidified with hydrochloric acid and the complex was precipitated from an ethanol-ether solution. The complex was filtered, washed with acidified ethanol and air dried. The chloride salt was characterized by comparing its infrared and visible spectra to that

of the iodide salt.

In Table 1 the pmr spectra of $[(NH_3)_5CoNHCOC_6H_5]^{2+}$ and $[(NH_3)_5CoNH_2COC_6H_5]^{3+}$ are shown. The spectrum of each is typical of the nitrogen bonded ligands showing the *cis* NH_3 protons separated from the *trans* NH_3 protons by 0.14 τ, with an intensity ratio of 4:1.

The low energy peaks in the electronic spectra, given in Table 2, show a decrease in λ_{max} in the order unprotonated amide > protonated amide > nitrile. This appears to be typical of other systems as well. The ultraviolet absorptions appear to be charge transfer bands and are difficult to assign.

The infrared spectrum of the unprotonated benzamide complex shows the typical absorptions of coordinated NH_3 groups. No C≡N stretch is observed in the alkaline hydrolysis product of the benzonitrile complex but an absorption at 1535 cm^{-1} may be assigned to the C=O stretch expected for the benzamide product. This frequency when compared to the free ligand C=O stretching frequency (1640 cm^{-1}) shows a low energy shift. The low energy shift has been rationalized in terms of the π-bonding in the N-C-O system.[1]

4. 4-Formylbenzonitrile Complex

$[(NH_3)_5CoNCC_6H_4CHO][ClO_4]_3$

A mixture of 5 gm of aquopentaamminecobalt(III) perchlorate, 20 gm of Linde 3A molecular sieves, and 2 gm of p-toluenesulfonic acid (1:1 molar ratio with the complex) and 50 ml of trimethyl-phosphate was stirred for 10 minutes in order to take up the water from the acid (monohydrate). Then 5 gm of 4-formylbenzonitrile was added and the mixture was heated in a paraffin oil bath at 80 ± 5°C for 4 hours. The resulting solution was filtered, cooled and added to 800 ml of sec-butyl alcohol which caused the crude complex to precipitate. The precipitate was recrystallized by dissolving it in a minimum amount of warm water, adding sodium perchlorate to produce a saturated solution and cooling. Further purification was carried out to remove any traces of p-toluenesulfonate by dissolving the complex in acidified water (40°C) then adding enough 62% $HClO_4$ to make the solution 1 M in $HClO_4$. Finally the solution was cooled and the product was collected by filtration. Isolation of the analytical grade product was carried out by cation exchange chromatography as described previously, using sodium chloride as the eluting agent.

Anal. Calcd for $[(NH_3)_5CoNCC_6H_4CHO][ClO_4]_3$: C, 16.74; N, 14.65; H, 3.49. Found: C, 16.89; N, 14.22; H, 4.04.

The pmr results are shown in Table 1 and the chemical shift difference of the *cis* and *trans* NH_3 protons indicates nitrogen bonding of the 4-formylbenzonitrile if the empirical rule previously discussed is applied.

The visible and ultraviolet absorption spectral data of the 4-formylbenzonitrile complex are given in Table 2. The spectrum shows the same features as the benzonitrile complex with the exception that the high energy absorption at 340-350 nm appears to be hidden underneath the extremely intense absorption of the ligand in the 4-formylbenzonitrile complex.

The characteristic vibrations of coordinated NH_3 are evident in the infrared spectrum of this complex. The C≡N stretching frequency of free 4-formylbenzonitrile occurs at 2230 cm^{-1}. Upon coordination to $(NH_3)_5Co^{3+}$ the C≡N stretching frequency shifts 60 cm^{-1} to higher wavenumber. This was similar to the increase found for the benzonitrile complex which was discussed previously.

The free C=O stretching frequency for the uncoordinated nitrile (1695 cm^{-1}) is not affected by complexation indicating that the 4-formylbenzonitrile is bonded through the cyano substituent.

5. The Conjugate Base of the N-isomer of 4-Formylbenzamidopentaamminecobalt(III), $[(NH_3)_5CoNHCOC_6H_4CHO]^{2+}$

The 4-formylbenzonitrile complex was dissolved in a minimum amount of warm alkaline water, and the pH was adjusted to ~9 by dropwise addition of sodium hydroxide. An excess of sodium iodide was added and the solution was placed in a refrigerator and cooled at -5°C for ~2 hr. The precipitate was collected by filtration, washed with ethanol, methanol, and ether, and finally air dried. The conjugate base of 4-formylbenzamidopentaamminecobalt-(III) iodide salt was recrystallized from alkaline warm water by the addition of sodium iodide. Ion exchange methods were not required as the product after recrystallization yielded analytical grade material.

Anal. Calcd for $[(NH_3)_5CoNHCOC_6H_4CHO][I]_2$: C, 17.59; N, 15.39; H, 3.85. Found: C, 17.60; N, 15.11; H, 3.92.

The pmr spectrum of the protonated and unprotonated 4-formylbenzamido complex is similar to that of the N-isomer of formamido- and acetamidopentaamminecobalt(III) perchlorate[1] in that both the *cis* and *trans* NH_3 protons occur at a single τ value as shown in Table 1. The formyl proton shift in the acidic and basic forms is similar to the corresponding shift in the nitrile form. The pmr spectrum thus indicates that the iodide salt is nitrogen bonded.

Further confirmation was achieved from the electronic spectra as the visible and ultraviolet absorptions are similar to that of $Co(NH_3)_6^{3+}$. The low energy peaks for the protonated and unprotonated 4-formylbenzamido and its respective nitrile complexes, as shown in Table 2, conform to an order noted previously. The 4-formylbenzamido complex shows the same features as the nitrile complex with the high energy d-d absorption hidden as before.

There is no C≡N stretch observed in the infrared spectrum of the 4-formylbenzamido complex, however, there is an absorption at 1695 cm^{-1} indicating the unbound C=O stretch of the formyl group. An absorption at 1550 cm^{-1} may be assigned to the carbonyl stretching frequency for the bound ligand

expected for the amide product. A comparison of the infrared spectra of the unprotonated amide complex and its corresponding nitrile complex shows that further new peaks appear at 1460 cm^{-1}, 1305 cm^{-1}, and 1250 cm^{-1} on formation of the carboxamido-pentaamminecobalt(III) salt.

(iii) Kinetic Measurements

1. Alkaline Hydrolysis

The alkaline hydrolysis of the benzonitrile complex was studied on an Aminco-Morrow stopped-flow system. The temperature of the reacting solutions was controlled by a Colora constant temperature bath by pumping water through the block that surrounded the drive syringes and the cell. The bath temperature was regulated by a Fisher Thermistemp controller, with the thermistor probe in contact with the block containing the drive syringes. The temperature of the solutions in the drive syringes was measured with a copper-constantan thermocouple. In all alkaline hydrolysis experiments reacting solutions were allowed to stand for fifteen minutes for temperature equilibration before the reaction was initiated.

The increase in absorbance was observed at 360 nm for the benzonitrile complex. A solution containing sodium hydroxide and sodium perchlorate, at a concentration to give a final ionic strength of 1.0 M, was mixed with a solution containing the benzonitrile complex dissolved in water. At each hydroxide ion concentration, between eight and ten traces of the transmittance change were recorded photographically, and the rate constants reported are an average obtained from these traces. The observed rate constants were determined by recalculating the observed transmittance results in absorbance units and by making a plot of log $(A_t - A_\infty)$ vs time, where A_t is the absorbance at time t and A_∞ is the absorbance at infinite time. The observed rate constant is obtained from the slope of this plot.

A second method was used for the alkaline hydrolysis of the 4-formylbenzonitrile complex. The reaction was followed on a Bausch and Lomb Precision Spectrophotometer. The spectrophotometer was equipped with the standard water circulation system previously described. The temperature of the reaction cell and its contents was controlled by pumping water from the constant temperature bath through a specially

designed aluminum block which surrounded the reaction cell in the spectrophotometer. The thermistor probe was placed in contact with the aluminum block keeping the temperature of the reacting solution constant during the course of the reaction.

The hydrolysis of the 4-formylbenzonitrile complex was followed by the decrease in absorbance with time in the ultraviolet spectra at λ = 290 nm. A solution containing sodium perchlorate and tris-(hydroxymethyl)-aminomethane buffer was adjusted to a pH between 7 - 8 by the dropwise addition of dilute $HClO_4$ while measuring the pH on a Beckman Expandomatic pH meter. The pH of the reaction mixture was measured before and after each kinetic run. The pH of the buffer solution was corrected for temperature effects and the temperature compensator on the pH meter was used. This buffer solution was mixed with a solution containing the cobalt(III)-nitrile complex and water. The resulting mixture gave a final ionic strength of 1.0 M. At each temperature between 10 and 15 kinetic runs of solutions at different pH values and constant ionic strength were followed. In several experiments the hydrolysis was followed at 520 nm but otherwise using the same procedure.

In addition, the alkaline hydrolysis of the 4-formylbenzonitrile complex was studied on an Aminco Morrow stopped-flow system at $[OH^-] = 0.01$ M at $\lambda = 290$ nm. At this hydroxide ion concentration, 14 traces of the transmittance change were recorded photographically and the rate constant reported is an average of these traces. The procedure used for preparing the 4-formylbenzonitrile complex reaction mixture for the stopped-flow technique was the same as that for the benzonitrile complex described previously. The observed rate constants in both the above methods were determined as before from a plot of log $(A_t - A_\infty)$ vs time.

2. Chromium(II) Reduction

High purity argon was used to deoxygenate the spectrophotometer cell containing the reagents for Cr(II) reductions. The cell was sealed with rubber serum caps. The chromium(II) solutions were handled and mixed using standard syringe techniques.

The reduction of the conjugate base N-isomer forms of benzamido- and 4-formylbenzamidopentaamminecobalt(III) complexes were studied on a Bausch and Lomb Precision Spectrophotometer equipped with the water circulating temperature control system

described in the previous section.

The reduction of the benzamido and the 4-formyl-benzamido complexes was followed by the decrease in absorbance with time at λ = 485 nm and 484 nm respectively. A reactant solution was prepared in a 5 cm cell containing the complex, perchloric acid at the required concentration, and lithium perchlorate to give a final ionic strength of 1.0 M. This solution was deoxygenated by passing pure argon through it, then the Cr^{2+} solution was added using the normal syringe procedures.

All reduction reactions were run under pseudo-first-order conditions (reductant in at least a 15 fold excess over oxidant). The observed rate constant was determined from the slope of a plot of log $(A_t - A_\infty)$ vs time, where A_t and A_∞ are the absorbances at time t and at infinite time respectively.

(iv) Ion Exchange of Reaction Mixtures

Reaction mixtures from reduction kinetic runs were ion exchanged immediately after the reaction was completed. The purpose of these experiments was to determine the amount of organic ligand transferred to the chromium(III) product. The

contents of the reaction cell were charged onto Dowex 50W-X12 cation exchange resin, in the hydrogen ion form, and separated at 5°C. The resin was pretreated with 50% acetone, ethanol, distilled water, 2 M sodium hydroxide, distilled water, 30% $HClO_4$ and distilled water in that order. This procedure was necessary since the resin decomposes slowly in air producing a product with an absorption in the ultraviolet region of the electronic spectrum.

The free ligand was eluted from the resin using 200 ml of water. All products were characterized spectrophotometrically on Cary Model 14 or Cary Model 15 Spectrophotometers. Benzamide (Eastman Kodak Co.) was characterized by eluting it through the cation exchange resin, recording its absorption in the ultraviolet region, and determining its extinction coefficient. Efforts to prepare pure 4-formylbenzamide failed and therefore a different method was used to characterize it. This method makes use of the fact that reduction of the cobalt(III) complex with vanadium(II) must result in release of all of the organic ligand because all the metal ion products are labile. The reduction of the 4-formylbenzamido complex with V^{2+} was followed to completion, and then the reaction mixture was

ion exchanged using water as the elutant. The ultraviolet spectrum was recorded and the extinction coefficient of 4-formylbenzamide was determined. The electronic spectra in the ultraviolet region of benzamide and 4-formylbenzamide are summarized in Table 3.

(v) Determination of Ionization Constant

The pK_a of the chloride salt of the benzamide complex was determined spectrophotometrically using a Bausch and Lomb Precision Spectrophotometer at a wavelength of 348 nm. Known volumes of 1.0 M hydrochloric acid were added to a solution of the complex in 14 ml of 1.0 M $LiClO_4$. The data were treated in the same manner as that used previously for carbamatopentaamminecobalt(III).[22] A similar attempt was made to determine the ionization constant of the iodide salt of the 4-formylbenzamido complex, however, the attempt was foiled by the limited solubility of the acidic form of the complex.

(vi) Instrumentation

The proton magnetic resonance spectra were obtained using a Varian 56/60 spectrophotometer. All visible and ultraviolet spectra were recorded

Table 3

Electronic Spectra of Free Organic Ligands[a]

Ligand	Absorption Maximum, nm (Extinction Coefficient, M^{-1} cm^{-1})	
Benzamide	268(6.8×10^2)[b]	225(9.2×10^3)[b]
4-formylbenzamide	250(1.1×10^4)[b]	

(a) All spectra are in aqueous solution unless otherwise noted.

(b) An average value was calculated from 3 determinations.

using Cary Model 14 or Cary Model 15 Spectrophotometers. The infrared spectra were obtained on a Perkin Elmer 421 grating spectrophotometer, using potassium bromide disks and Nujol mulls. The pH measurements were made on a Beckman Expandomatic pH meter.

CHAPTER III

RESULTS AND DISCUSSION

(i) Alkaline Hydrolysis Reaction

As noted in the introduction section the hydrolysis of the coordinated nitrile to its respective coordinated amide (I-3) was carried out in aqueous alkaline solution. The hydrolysis rate of the pentaamminecobalt(III) complexes of both benzonitrile and 4-formylbenzonitrile followed the rate law:

$$\frac{-d \ln [complex]}{dt} = k_{obsd} = k_1[OH^-] \qquad (III-1)$$

The results of the kinetic study are given in Table 4 and Table 5 and a typical plot of k_{obsd} versus hydroxide ion concentration is shown in Figure 1. A summary of the kinetic results and the activation parameters is given in Table 6. The activation parameters of both the alkaline hydrolysis and the Cr^{2+} reduction reactions were determined using the transition state equation:[23]

$$\log \left(\frac{k}{T}\right) = - \frac{\Delta H^{\ddagger}}{2.303\ R} \left(\frac{1}{T}\right) + \left[\frac{\Delta S^{\ddagger}}{2.303\ R} + \log\left(\frac{\kappa k_B}{h}\right)\right]$$

where k is the specific rate constant in $M^{-1}sec^{-1}$,

k_B is Boltzmann's constant, T is the temperature in °K, κ is the transmission coefficient, h is Planck's constant, R is the gas constant in cal deg^{-1} $mole^{-1}$, $\Delta H^{\ddagger}$ is the enthalpy of activation and $\Delta S^{\ddagger}$ is the entropy of activation. A plot of $\log \left(\frac{k}{T}\right)$ versus T^{-1} should be a straight line with slope $- \frac{\Delta H^{\ddagger}}{2.303\ R}$ and intercept $\frac{\Delta S^{\ddagger}}{2.303\ R} + \log \frac{k_B}{h}$ where κ is assumed to be unity.

Evidence will now be considered that indicates that reaction scheme (III-2) is followed for the alkaline hydrolysis reaction of the nitrile coordinated complexes.

$$(NH_3)_5CoN{\equiv}C\text{-}C_6H_4\text{-}X^{3+} + OH^- \rightarrow (NH_3)_5CoNHC(=O)\text{-}C_6H_4\text{-}X^{2+} \qquad \text{(III-2)}$$

The products from the benzonitrile and 4-formyl-benzonitrile complexes where X = H, CHO respectively, have been isolated and the chemical analysis and the pmr spectrum are as expected for a N-bonded amide complex. The infrared spectrum of each product shows that the C≡N stretching mode has been lost and an absorption can be assigned to the C=O stretching vibrations expected for the carboxamide product.

The alkaline hydrolysis reaction of the 4-formyl-benzonitrile complex was followed at two wavelengths

TABLE 4

Kinetic Results for the Hydrolysis of the Benzonitrile Complex of Pentaamminecobalt(III)[a]

Temp. °C	$[OH^-]$ M	k_{obsd} sec^{-1}	k_1 $M^{-1}sec^{-1}$
25.6	0.05	0.901	18.0
25.6	0.125	2.38	19.0
25.6	0.250	4.75	19.0
40.4	0.05	3.53	70.5
40.4	0.15	11.6	77.5

(a) Studied at 1.0 M ionic strength in $NaClO_4$.

TABLE 5

Kinetic Results for the Hydrolysis of the 4-Formylbenzonitrile Complex of Pentaamminecobalt(III)[a]

Temp °C	pH	$[OH^-]^b$ M x 10^6	k_{obsd} sec^{-1} x 10^3	k_1 $M^{-1}sec^{-1}$
25.0	7.93	1.46	0.34	233
25.0	8.28	3.27	0.85	260
25.0	8.34	3.75	0.95	253
25.0	8.41	4.41	1.07	243
25.0	8.50	5.43	1.41	260
25.0	8.57	6.38	1.57	246
25.0	8.59	6.68	1.92	288
25.0	8.64	7.49	1.92	256
25.0	8.70	8.60	2.45	285
25.0	8.76	9.87	2.70	273
25.0	8.82	11.34	3.14	277
25.0	8.86	12.43	3.30	265
25.0	8.90	13.63	3.38	248
25.0	8.00[c]	1.72	0.43	251
25.0	(12.00)[d]	0.01 x 10^6	3.17 x 10^3	317
35.0	8.00	3.64	1.99	547
35.0	8.13	4.91	2.66	542
35.0	8.26	6.62	3.21	485
35.0	8.30	7.26	2.92	402
35.0	8.36	8.34	4.20	504
35.0	8.41	9.35	4.03	431
35.0	8.44	10.02	5.63	562
35.0	8.52	12.05	6.93	575
35.0	8.54	12.62	6.86	544
35.0	8.54	12.62	6.66	528
35.0	8.66	16.63	8.15	490

Table 5 (con't)

Temp °C	pH	$[OH^-]^b$ M x 10^6	k_{obsd} sec^{-1} x 10^3	k_1 $M^{-1}sec^{-1}$
35.0	8.76	20.94	10.19	487
35.0	8.78	21.93	10.66	486
40.0	7.18	0.078	0.69	887
40.0	7.62	2.14	1.77	826
40.0	7.70	2.58	1.97	765
40.0	7.74	2.82	2.32	821
40.0	7.78	3.10	2.22	717
40.0	7.80	3.24	2.41	743
40.0	7.87	3.81	2.64	693
40.0	7.88	3.90	3.00	769
40.0	7.95	4.58	3.57	779
40.0	7.98	4.91	3.65	744
40.0	7.99	5.02	3.89	774
40.0	8.08	6.18	4.95	801
40.0	8.09	6.32	4.81	761
40.0	8.09	6.32	4.53	716
40.0	8.16	7.43	5.25	707

(a) Studied at 1.0 M ionic strength in $NaClO_4$.

(b) Hydroxide ion activity, calculated from the measured value of K_w at 25° in 1 M $NaClO_4$[24], and assuming the temperature dependence of K_w is the same in 1 M NaCl[26] and $NaClO_4$; 10^{14} x K_w = 1.716 (25°), 3.639 (35°), 5.140 (40°).

(c) Kinetic run at λ = 520 nm.

(d) Studied in 0.01 M NaOH and 1 M $NaClO_4$.

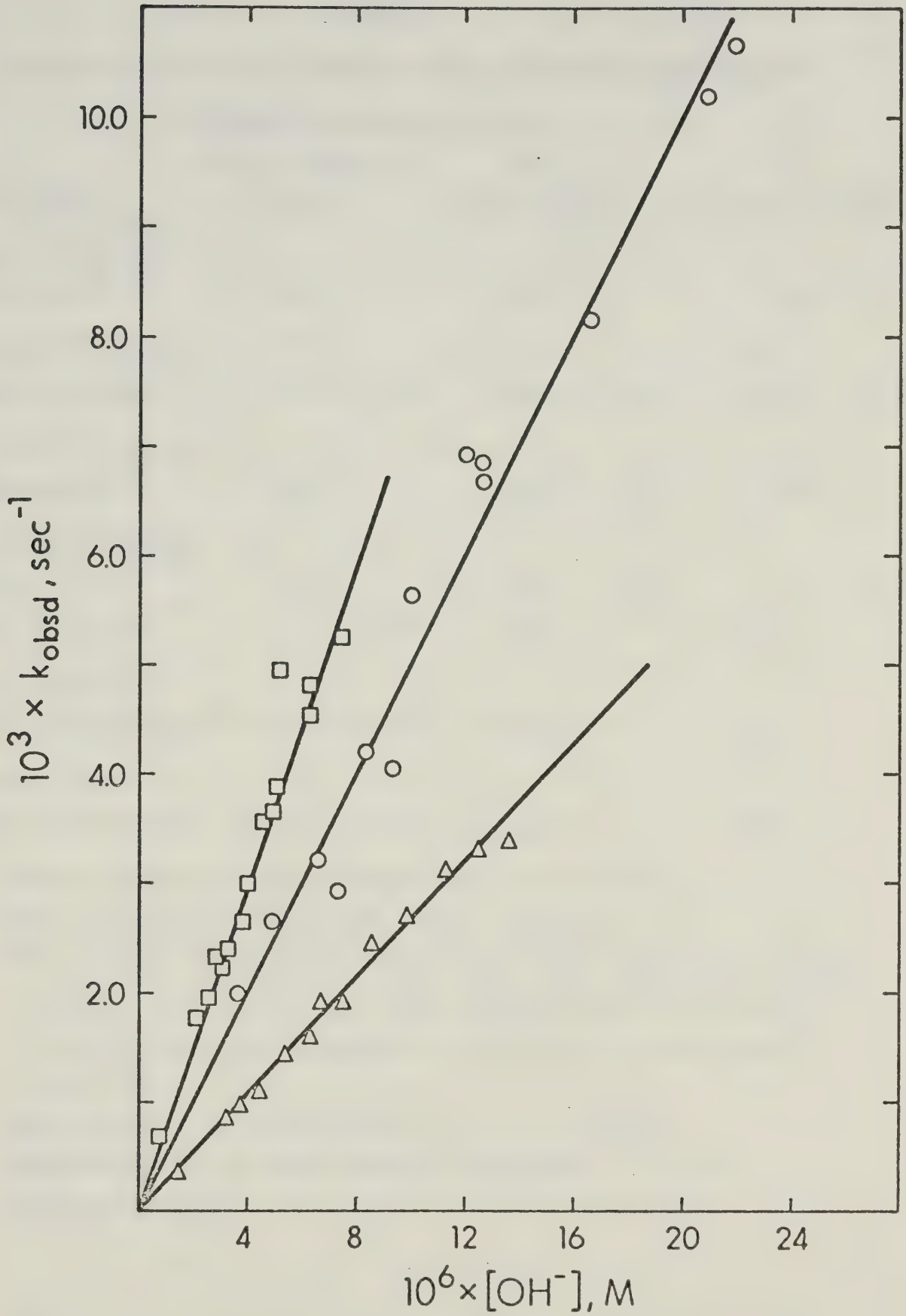


Figure 1. Dependence of the Hydrolysis Rate of the 4-Formylbenzonitrile Complex of Pentaammine-cobalt(III) on $[OH^-]$, Ionic Strength 1.0 M ($NaClO_4$): △, 25.0°; ○, 35.0°; □, 40.0°C.

TABLE 6

Summary of Kinetic Results for Alkaline Hydrolysis of Coordinated Nitriles

Compound	Rate Constant[a] $M^{-1}sec^{-1}$	$\Delta H^{\ddagger}$ kcal $mole^{-1}$	$\Delta S^{\ddagger}$ cal $mole^{-1}deg^{-1}$
$(NH_3)_5Co(benzonitrile)^{3+}$ [b]	18.9	16.5	2.6
$(NH_3)_5Co(4\text{-formylbenzonitrile})^{3+}$ [b]	2.73×10^{2} [c]	12.6 ± 1.4	-5.2 ± 4.5
$(NH_3)_5Co(4\text{-cyanophenoxide})^{2+}$ [d]	0.18	16.3 ± 1.5	-7.4 ± 4
$(NH_3)_5Co(3\text{-cyanophenoxide})^{2+}$ [d]	3.57	15.1 ± 1.5	-5.5 ± 4
Benzonitrile[e]	8.2×10^{-6}	19.9	-15.2
Ni(2-cyano-1,10-phenanthroline)$^{2+}$ [f]	2.4×10^{4}	15.1	14
2-cyano-1,10-phenanthroline[f]	2.6×10^{-3}	15.7	-20

(a) Rate constants calculated for T = 25.6°C.

(b) This work in $NaOH\text{-}NaClO_4$ at μ = 1.0 M.

(c) This value is recalculated from the transition state equation for the activation parameters calculated from the rate constants at T = 25.0°C (2.63×10^{2} $M^{-1}sec^{-1}$).

(d) Reference 6 in $NaOH\text{-}NaClO_4$ at μ = 1.0 M.

(e) Reference 13 in 50% aqueous acetone.

(f) Reference 14.

as described earlier. The reaction was followed at 520 nm in order to determine if a reaction was occurring at a site near or remote from the $Co(NH_3)_5^{3+}$ moiety. The alkaline hydrolysis reaction scheme (III-2) will affect the nitrile coordinate bond to the Co(III) metal center and thus should have a direct affect on the absorption at 520 nm (this absorption is due to a d-d transition). On the other hand, the hydration of the aldehyde group, a group remote from the Co(III) center, is likely to have little effect on the Co^{3+} center and on the absorption at 520 nm. Hydration of the aldehyde group should cause a marked change in the absorption at 290 nm as this is the charge transfer region involving electronic levels on the ligand. Since the rate constants determined at the different wavelengths were similar it is concluded that the observations are not associated with the hydration of the remote aldehyde group.

One hydrolysis run on 4-formylbenzonitrile was done at 0.01 M NaOH on the stopped-flow instrument at 290 nm. This run provides a rate constant in terms of concentration, instead of in terms of activity, and is therefore more directly comparable to values from the previous work on the benzonitrile complex. The ratio of the activity and concentration

rates is 0.83, a reasonable value for the activity coefficient of sodium hydroxide in 1.0 M $NaClO_4$. The rather small rate constant difference certainly would not indicate that a different reaction was being observed in 0.01 M NaOH than at pH 7-8.

Table 6 shows that the rate of alkaline hydrolysis of the 4-formylbenzonitrile complex is approximately 14 times greater than that of the benzonitrile complex. This rate difference may be a reflection of a change in electron distribution within the ligand brought about by the electron withdrawing formyl group. A -CHO group is known to be a strongly electron withdrawing substituent.[27] Thus nucleophilic attack at the -CN group by hydroxide ion is enhanced by the formyl substituted ligand.

It has been found previously[13] that nitrile hydrolysis rate constants show a linear free energy relationship. This is also true for the coordinated nitriles studied here for which, at 25.6°

$$\log k = 4.22\sigma + 1.34$$

This relationship is also followed by the 3- and 4-cyanophenol complexes.[17] The σ values[28] of -0.52, -0.19, 0.00 and 0.22 have been used for para and meta O^-, -H and para-CHO substituents,

respectively.

Coordination to a $(NH_3)_5Co^{3+}$ moiety increases the rate of benzonitrile hydrolysis by a factor of ~2 x 10^6 as can be seen from Table 6. The cobalt(III) system gives both a more favorable $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and, at least in the benzonitrile system, both factors contribute about equally to the net increase in rate. This behavior may be contrasted to that of the nickel(II) system studied by Breslow *et al*[14] in which the rate increase is essentially due to a more favorable $\Delta S^{\ddagger}$. Breslow has argued that this is associated with bonding of the developing imino ion to the metal in the transition state. Such an effect will not operate in the $(NH_3)_5Co^{3+}$ systems because the imino group is already coordinated to Co(III).

(ii) Acid Dissociation Constant of $(NH_3)_5CoNH_2\overset{O}{\overset{\|}{C}}-C_6H_5^{3+}$

The effect of changing hydrogen ion concentration on the spectrum of the N-isomer of benzamidopentaamminecobalt(III) is interpreted in terms of the equilibrium (III-3).

$$(NH_3)_5CoNH_2\overset{O}{\overset{\|}{C}}C_6H_5^{3+} \rightleftarrows (NH_3)_5CoNH\overset{O}{\overset{\|}{C}}C_6H_5^{2+} + H^+ \qquad \text{(III-3)}$$

Considerable evidence has been adduced in support of the predominance of both O-protonation and N-protonation of amides. There has been a general agreement that O-protonation is predominant in strong acid media.[7,9,10,11] However, Liler[11,12] has recently suggested that tautomeric equilibrium exists in which the N-protonated species exists in dilute aqueous acid and the O-protonated species exists in concentrated acid. The reaction (III-3) is similar to that found for the N-bonded formamide complex.[29] The main evidence for N-protonation of the formamide complex is the large difference in the visible spectra of the complex on going from water to an acidic solution. It was felt that protonation of the carbonyl oxygen, a group remote from the Co(III) metal center, would have little effect on the absorption in the visible spectra of the complex. A similar large difference in the visible spectra of the benzamido complex was noted in this work, suggesting that the proton was not being removed from a site remote from the $(NH_3)_5Co^{3+}$ moiety.

The pmr studies did not help to establish the site of protonation because resonances due to -NH and $-NH_2$ protons were too weak to be definitely

assigned. The pmr spectrum of the protonated form produced by adding trifluoracetic acid to a DMSO solution of $(NH_3)_5CoNHCOC_6H_5^{2+}$ showed signs of rearrangement to the O-bonded isomer. The peaks of the *trans*- and *cis*-NH_3 protons had a chemical shift difference of ~1.2τ after a period of ~24 hr at room temperature, well within the empirical rule established previously for an O-bonded complex. This rearrangement also interfered with the assignments of the -NH and $-NH_2$ proton peaks. Further investigations of the site of protonation are being done by pmr studies of the acetamide complex,[30,31] but these are also complicated by solvolysis problems.

For a system such as the protonation of the benzamide complex, the pK_a may be determined spectrophotometrically by applying the following equation[1]

$$\frac{A_{obsd} - A_R}{[H^+]} = \left(-\frac{1}{K_a}\right) A_{obsd} + \frac{A_{RH}}{K_a}$$

where A_R, A_{RH}, and A_{obsd} are the absorbance due to the unprotonated species, protonated species and the total observed absorbance respectively and K_a is the acid dissociation constant. A plot of $(A_R - A_{obsd})[H^+]^{-1}$ versus A_{obsd} yields a straight

line with slope K_a^{-1}. The data at 25°C given in Table 7 are plotted in Figure 2. The pK_a values at 16°, 25°, and 35° measured spectrophotometrically at 348 nm are 1.80, 1.65, and 1.49, respectively. These are the average values from five determinations at each temperature. The enthalpy and entropy of reaction (III-3) are 6.7 ± 0.6 kcal $mole^{-1}$ and 14.8 ± 2.0 e.u. respectively. The measured pK_a values for reaction (III-3) are smaller than those for the formamido complex,[1] possibly due to stabilization of the conjugate base by conjugation with the benzene ring. It is noteworthy that the enthalpy and entropy for the proton dissociation reaction of the formamido complex, -4.6 kcal $mole^{-1}$ and -25 e.u. respectively, are quite different from those of the benzamido complex.

Coordination to $(NH_3)_5Co^{3+}$ has changed the pK_a of benzamide (at 25°C) from 14[27] to 1.65 or about 12 pK_a units. Similar changes are noted for the N-bonded linkage isomers of sulfamate and formamide,[1] > 10 and > 13 pK_a units respectively. Thus the change in pK_a may provide some evidence for formulating the complex as the nitrogen bonded ligand.

TABLE 7

Equilibrium Data for the Spectrophotometric Determination of the Dissociation Constant of $(NH_3)_5CoNH_2\overset{O}{\overset{\|}{C}}C_6H_5^{3+}$ at 25.0°C[a,b]

Volume of Solution, ml	$[H^+]$, M	A_{obsd}	$(A_R - A_{obsd})[H^+]^{-1}$ M^{-1}
14.00	---	0.900	---
14.10	0.0071	0.846	7.61
14.15	0.0106	0.828	6.79
14.20	0.0141	0.814	6.10
14.25	0.0175	0.802	5.60
14.30	0.0210	0.795	5.00
14.35	0.0244	0.784	4.75
14.40	0.0278	0.779	4.35
14.45	0.0311	0.774	4.05
14.50	0.0345	0.767	3.86

(a) Ionic strength μ = 1.00 M ($LiClO_4$).

(b) Total complex concentration is 0.0016 M in a 5 cm cell.

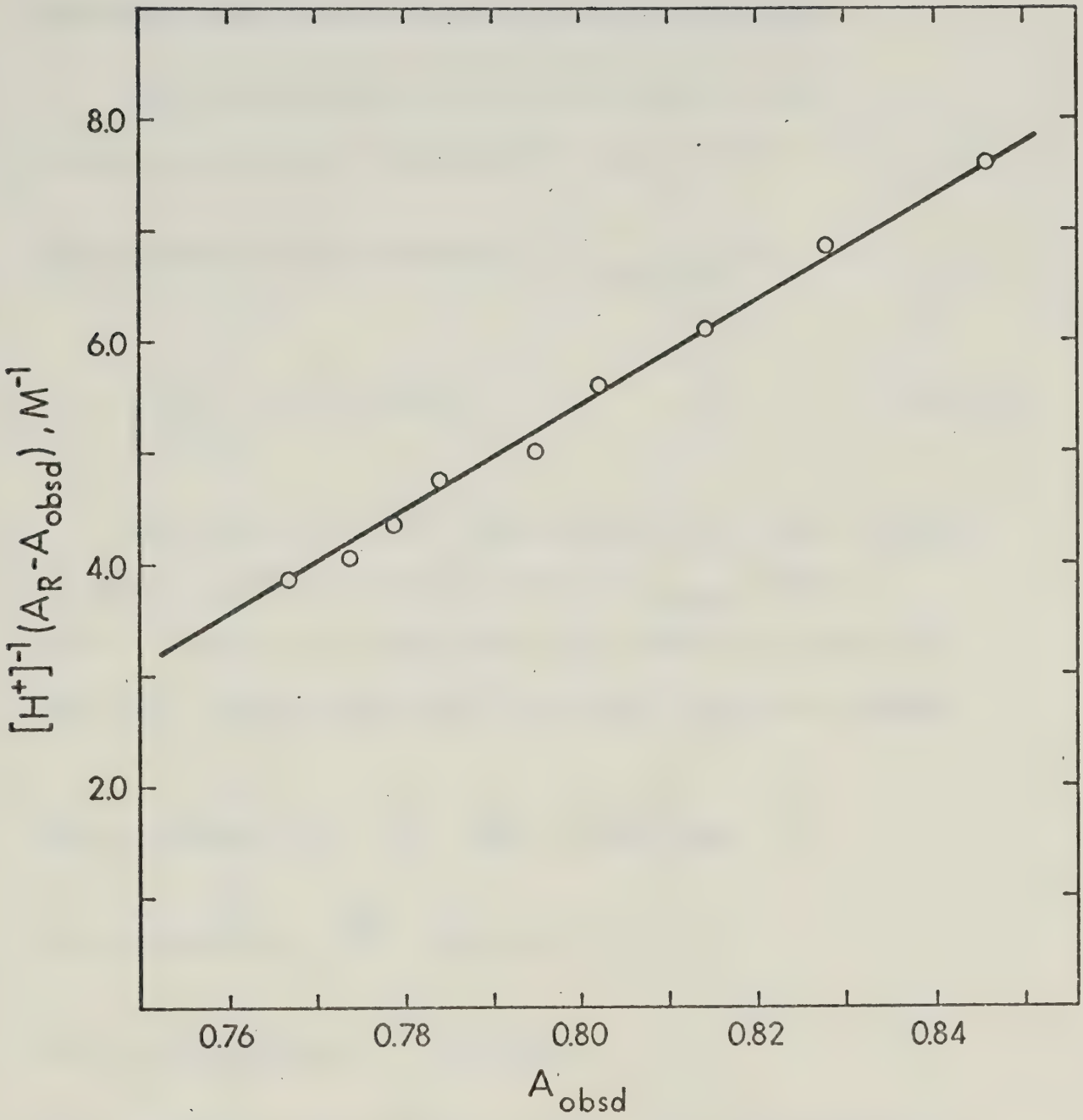


Figure 2. Determination of the Acid Dissociation Constant (K_a) for $(NH_3)_5CoNH_2\overset{O}{\overset{\|}{C}}C_6H_5^{3+}$ from the Change in Absorbance at λ = 348 nm at 25°C, Ionic Strength 1.00 M ($LiClO_4$): A_R is the absorbance due to $(NH_3)_5CoNH\overset{O}{\overset{\|}{C}}C_6H_5^{2+}$ and A_{obsd} is the observed absorbance.

(iii) Chromium(II) Studies: Kinetics and Product Analysis for Benzamidopentaamminecobalt(III)

The chromium(II) reduction rate of the benzamido complex followed the rate law:

$$\frac{-d(\ln[\text{cobalt(III) complex}])}{dt} = k_{obsd}[Cr^{2+}]$$

$$= \left(\frac{k_1'}{[H^+]} + k_2' \right) [Cr^{2+}] \qquad \text{(III-4)}$$

The rate data for the reduction of this complex is given in Table 8 and plots of k_{obsd} versus $[H^+]^{-1}$ at 25°, 35° and 45°C are shown in Figure 3. The rate law is consistent with the reaction scheme

$$(NH_3)_5CoNH_2\overset{O}{\overset{\|}{C}}C_6H_5 \overset{K_a}{\rightleftharpoons} (NH_3)_5CoNH\overset{O}{\overset{\|}{C}}C_6H_5 + H^+$$

$$(NH_3)_5CoNH\overset{O}{\overset{\|}{C}}C_6H_5 \overset{k_1}{\rightleftharpoons} \text{products}$$

$$(NH_3)_5CoNH_2\overset{O}{\overset{\|}{C}}C_6H_5 \overset{k_2}{\rightleftharpoons} \text{products}$$

The products are $Co^{2+}(aq)$, NH_4^+, and a chromium(III) complex. This mechanism gives the rate law

$$\frac{-d(\ln[\text{cobalt(III) complex}])}{dt} = \left(\frac{k_1 K_a}{K_a + [H^+]} + \frac{k_2[H^+]}{K_a + [H^+]} \right) [Cr^{2+}]$$

(III-5)

TABLE 8

Kinetic Results for the Reduction of Benzamidopentaamminecobalt(III)[a]

Temp. °C	$[Co^{3+}]x10^3$ M	$[Cr^{2+}]x10^2$ M	$[H^+]$ M	$k_{obsd}x10^2$ sec^{-1}
25	0.80	4.13	0.050	0.55
25	0.80	4.05	0.067	0.50
25	0.80	3.99	0.10	0.45
25	0.80	4.03	0.20	0.40
25	0.80	4.11	0.50	0.37
35	0.80	4.09	0.050	1.27
35	1.60	3.87	0.056	1.26
35	1.60	4.13	0.067	1.14
35	1.60	4.13	0.10	0.97
35	1.60	5.80	0.20	0.82
35	0.80	4.09	0.50	0.76
35	1.60	4.13	0.50	0.73
45	1.61	3.87	0.050	2.80
45	0.81	4.10	0.067	2.52
45	1.60	3.80	0.067	2.50
45	1.60	3.47	0.10	2.19
45	1.60	3.87	0.20	1.87
45	0.80	4.12	0.20	1.83
45	1.60	4.60	0.50	1.69
45	0.80	4.10	0.50	1.72

(a) The ionic strength was kept at 1.0 M with lithium perchlorate for all kinetic experiments.

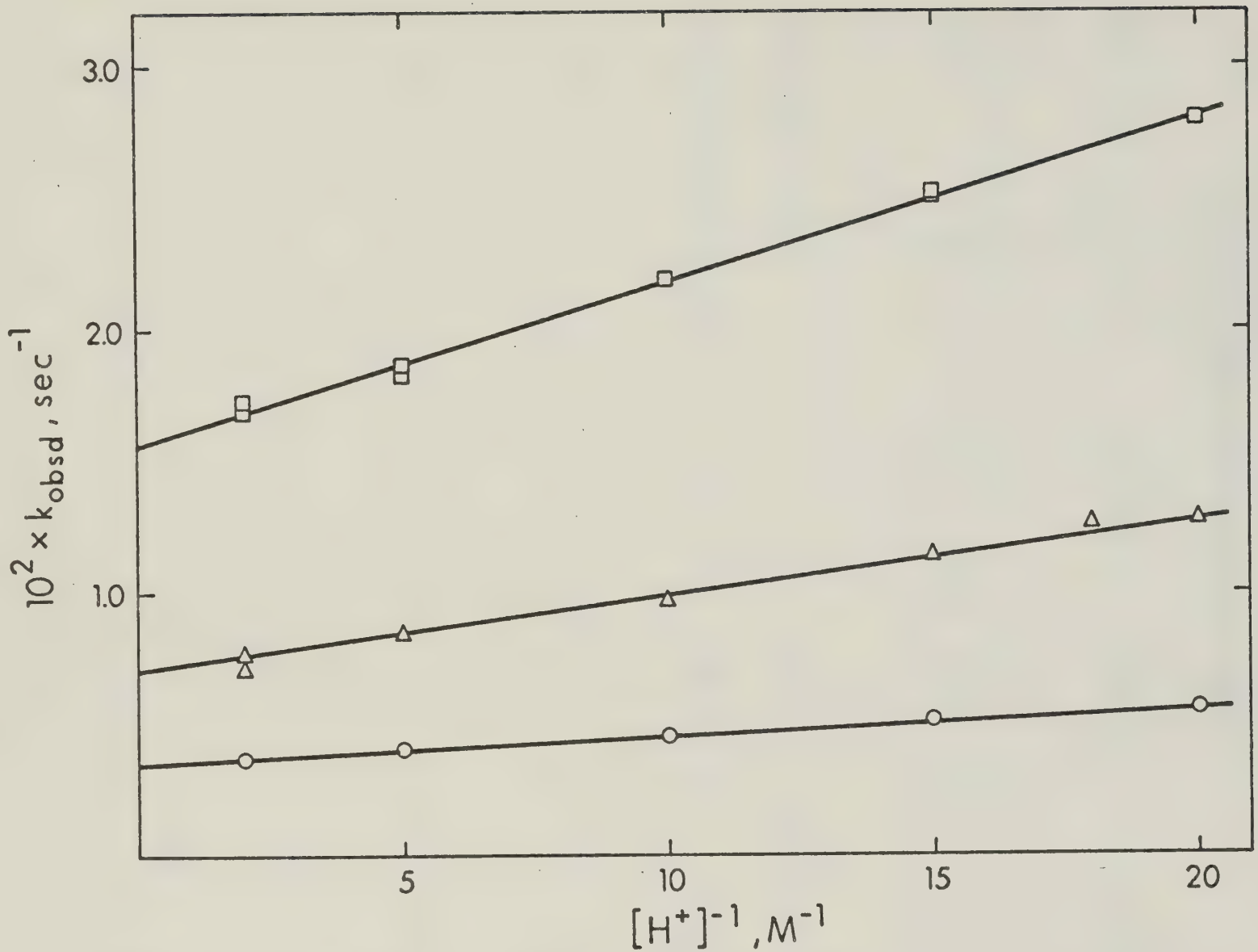


Figure 3. Dependence of the Reduction Rate of the Benzamidopentaamminecobalt(III) Complex by Cr^{2+} on $[H^+]$, Ionic Strength 1.0 M ($LiClO_4$): ○ , 25.0°; △, 35.0°; □, 45.0°.

TABLE 9

Kinetic Parameters for the Reduction of Benzamidopentamminecobalt(III)

Temp. °C	pK_a	k_1K_a sec^{-1}	k_1 $M^{-1}sec^{-1}$	k_2 $M^{-1}sec^{-1}$
25	1.65	1.00×10^{-4}	0.45×10^{-2}	0.35×10^{-2}
35	1.49	2.77×10^{-4}	0.84×10^{-2}	0.71×10^{-2}
45	1.34	6.21×10^{-4}	1.37×10^{-2}	1.56×10^{-2}
$\Delta H^{\ddagger}$ kcal $mole^{-1}$			10.1 ± 1.7	13.4 ± .9
$\Delta S^{\ddagger}$ cal $mole^{-1}deg^{-1}$			-35.3 ± 5.7	-24.7 ± 2.9

Under the conditions of the kinetic study $[H^+] >> K_a$; it can be seen that equations (III-4) and (III-5) are equivalent. The specific rate constants have been determined from the plot of k_{obsd} vs $[H^+]^{-1}$; yielding a slope of k_1K_a and an intercept of k_2. Since the K_a values are known the k_1 values have been calculated and entered in Table 9 along with the values of k_2 and their respective activation parameters.

In general it has been found that kinetic parameters alone are not sufficient to establish the electron transfer mechanism. The identification of the initial products of the reduction reaction is of utmost importance in determining the mechanism of the reaction and the point of attack of the reductant. The existence of a chromium(III) ligand complex where the ligand was originally coordinated to the cobalt(III) center is conclusive evidence for an inner-sphere mechanism. However, the lack of a ligand transfer complex does not mean that an inner-sphere mechanism is not operating. The latter may be the result of a fast hydrolysis reaction of the chromium(III) complex to $Cr(H_2O)_6^{3+}$. However, pentaaquochromium(III) complexes are normally stable with respect to hydrolysis.[32]

The analysis of the products of the reaction of the benzamido cobalt(III) complex forms a very important part of the study of the reduction of this complex. The percentage of ligand transfer was obtained by spectrophotometrically determining the amount of the uncoordinated ligand after reaction since it was very difficult to separate the ligand transfer complex from the relatively large amounts of $Cr(H_2O)_6^{3+}$. The electronic spectrum of the uncoordinated ligand recovered from the reaction solution, after cationic exchange chromatography, showed that no chemical change had occurred to the ligand. A blank experiment was carried out in which uncoordinated benzamide was substituted for co-ordinated benzamide in the reaction mixture and the solution was ion exchanged. The free benzamide was recovered completely from the experiment. Therefore no retention of the ligand by the ion exchange resin occurred. The percentages of the uncoordinated benzamide are tabulated in Table 10, and the mean percentage recovered is 88.7%.

In further experiments the hydrolysis of the Co(III) benzamido complex was studied at 45°C. At $[H^+]$ = 0.0345 M and 0.50 M the rates of hydrolysis were 1.31×10^{-4} sec^{-1} and 3.07×10^{-4} sec^{-1}

TABLE 10

Percent Free Benzamide Recovered after the Reduction Reactions

Temp. °C	$[Cr^{2+}]x10^{2}$ M	$[H^{+}]$ M	$[Co^{3+}]x10^{3}$ M	Percentage Free Benzamide Recovered
25	4.13	0.050	0.80	89.2
25	3.99	0.10	0.80	88.4
35	3.87	0.056	1.60	90.0
35	5.80	0.20	1.60	85.0
35	4.13	0.50	1.60	87.5
45	3.87	0.050	1.61	87.7
45	3.87	0.056	1.60	90.0
45	3.47	0.10	1.60	88.4
45	3.87	0.20	1.60	91.7
45	4.60	0.50	1.60	89.2

respectively. A comparison of the hydrolysis half-times to the Cr(II) reduction half-times at 45°C (2260 sec:900 sec and 5280 sec:600 sec at $[H^+]$ = 0.50 M and $[H^+]$ = 0.0345 M respectively) shows that very little hydrolysis of the Cr(III) product should occur during the time span of the reduction reaction, if the rate of hydrolysis of the Cr(III) product is similar to the hydrolysis of the Co(III) complex.[33] It must be noted, however, that the Cr^{2+} reduction with ligand transfer may yield the O-bonded Cr^{3+} complex $(H_2O)_5Cr\text{-}O{=}\overset{NH_2}{\overset{|}{C}}\text{-}C_6H_5^{3+}$. Thus a comparison of hydrolysis rates is not strictly justified if the bonding mode is different at Cr(III) than at Co(III). In general it is found, as discussed in the introduction, that amides prefer O-coordination so that the O-bonded form would be more stable than the protonated N-bonded form. Thus the rate comparison of Co^{3+} and Cr^{3+} systems would be a conservative one in that it probably overestimates the hydrolysis rate of the chromium(III) species. In addition, the data indicates the free ligand recovered is independent of the hydrogen ion and the temperature. At higher temperature hydrolysis would be more important, because hydrolysis reactions of chromium(III)

complexes have larger $\Delta H^{\ddagger}$ values (> 20 kcal $mole^{-1}$) than the Co(III)-Cr(II) reduction reactions (< 14 kcal $mole^{-1}$). Therefore less transfer would be expected at higher temperatures if hydrolysis were important. The data also demonstrates that release of ligand is insensitive to the concentrations of Co(III) and Cr(II) used in the experiment. If hydrolysis of the Cr(III) product were occurring the % transfer should show a trend with initial Cr^{2+}, because increasing the latter increases the rate of reduction but not the rate of hydrolysis, so that more transfer could be seen at higher initial $[Cr^{2+}]$ if there were hydrolysis. Studies of the aquation of the chromium(III) carboxamide complexes of nicotinamide and isonicotinamide also indicate that hydrolysis should be unimportant for the benzamide system. The former systems have hydrolysis rate constants of ~6×10^{-5} sec^{-1} at 25°C and the positive charge on the pyridine ring should make hydrolysis faster than for benzamide.

However, there is the added complication of Cr^{2+} catalyzed hydrolysis of the ligand transfer complex. This might occur via the reaction scheme (III-6).

$$(H_2O)_5Cr^{3+}O{=}C(NH_2)\text{-}C_6H_5 + Cr^{2+}(H_2O)_6 \xrightarrow{\text{outer sphere}}$$

$$(H_2O)_5Cr^{2+}\text{-}O{=}C(NH_2)\text{-}C_6H_5 + Cr^{3+}(H_2O)_6$$

$$\underset{\text{labile}}{(H_2O)_5Cr^{2+}\text{-}O{=}C(NH_2)\text{-}C_6H_5} \xrightarrow{\text{fast}} Cr^{2+} + O{=}C(NH_2)\text{-}C_6H_5 \qquad \text{(III-6)}$$

However, Cr^{2+}-Cr^{3+} reductions are normally only significant subsequent reactions when some change in bonding mode occurs for the bridging ligand, as in Nordmeyer's[3] case with isonicotinamide where

$$(H_2O)_5Cr^{3+}O{=}C(NH_2)\text{-}\langle O\,N \rangle + Cr^{2+}(H_2O)_6 \xrightarrow{\text{moderately fast}}$$

$$Cr^{2+}(H_2O)_6 + O{=}C(NH_2)\text{-}\langle O\,N \rangle\text{-}Cr^{3+}(H_2O)_5$$

The above reaction would still yield an inner-sphere ligand transfer product and this subsequent reaction would have no effect on the amount of free ligand collected immediately following the reduction reaction. In order to have ligand release catalyzed by Cr^{2+} one must have an outer-sphere mechanism operating for the benzamido chromium(III) product. The study of Deutsch and Taube[34] yields a value for

k_{obsd} of 1 x 10^{-4} sec^{-1} (25°C) for the Cr^{2+} catalyzed aquation of acetatopentaaquochromium(III). Observed rate constants for the cobalt(III) reduction in the present work are ~5 x 10^{-3} sec^{-1} (25°C) and therefore it is unlikely that the outer-sphere Cr^{2+} catalyzed aquation would occur rapidly enough to cause an error in the product analysis.

In summary it appears that subsequent reactions should not interfere with the product analysis. Therefore the reduction of the benzamidopentaammine-cobalt(III) complex proceeds with ~11% ligand transfer to chromium(III).

Any mechanism postulated for the reduction of the benzamido complex of pentaamminecobalt(III) by Cr(II) must explain not only the observed kinetic results but also the results of the product analyses. The possibility of either a strictly outer-sphere or strictly inner-sphere pathway seems unlikely here, as a result of the ~11% ligand transfer product. A possible mechanism is one that involves two distinct pathways, a normal outer-sphere reaction as the major pathway together with a much smaller inner-sphere pathway. This mechanism as a possible explanation of the experimental data will now be considered.

In a normal outer-sphere mechanism the ligand coordinated to the cobalt(III) center formally takes no part in the detailed electron transfer mechanism. The transfer of the electron is directly from an orbital of the reductant into an orbital of the oxidant. It may be true, however, that increased delocalization of the electron on the reductant caused by a large conjugated ligand may make electron transfer to the oxidant more facile.[5]

The acetonitrile complex,[35] $(NH_3)_5CoNCCH_3^{3+}$, and the hexaammine complex,[36] $Co(NH_3)_6^{3+}$, have been studied and their respective rates of reduction by chromium(II) were found to be 0.017 $M^{-1}sec^{-1}$ and $10^{-4}M^{-1}sec^{-1}$. These reactions must proceed by outer-sphere mechanisms since there is no group on the oxidant with a pair of electrons available to form the bridged species with the reductant. The rate of the reduction of the unprotonated or the protonated benzamido complex (k_1 = 4.5 x 10^{-3} $M^{-1}sec^{-1}$, k_2 = 3.5 x 10^{-3} $M^{-1}sec^{-1}$) are similar to but slower than the rate of outer-sphere reduction of the acetonitrile complex. Therefore from the rate constants it seems reasonable that the benzamido system may proceed by a major outer-sphere pathway with a small ligand transfer path. However, which particular

mechanism is operating may not be decided solely on a rate comparison. Similarly activation parameters cannot be used as being definitive of a mechanism. It has been observed[1] that, as a general rule, reduction should not be considered as proceeding by a simple outer-sphere path if the activation energy is less than 11 kcal $mole^{-1}$ and if the entropy is more negative than -30 cal $mole^{-1}deg^{-1}$. The activation parameters for the unprotonated path and the protonated path of the benzamido complex are $\Delta H_1^{\ddagger}$ 10.1 kcal $mole^{-1}$ and $\Delta S_1^{\ddagger}$ -35 cal $mole^{-1}deg^{-1}$, $\Delta H_2^{\ddagger}$ 13.4 kcal $mole^{-1}$ and $\Delta S_2^{\ddagger}$ - 25 cal $mole^{-1}deg^{-1}$ respectively. The unprotonated path seems to parallel an inner-sphere reduction as with benzoato[36] ($\Delta H^{\ddagger}$ 9.0 kcal $mole^{-1}$, $\Delta S^{\ddagger}$ -33 cal $mole^{-1}deg^{-1}$) whereas the protonated path follows the general rule above, suggesting that it proceeds by an outer-sphere mechanism. In Table 11 are shown the percentage of reaction proceeding by the k_1' path (unprotonated path). As the $[H^+]$ is increased the amount proceeding by the k_1 path is decreased. If the inner-sphere ligand transfer product was due solely to the k_1' path the amount of ligand transfer product should also vary in a like manner with $[H^+]$. However, the product analysis does not substantiate that

TABLE 11

Percentage of Reduction Proceeding by Unprotonated Path

Temp. °C	$[H^+]$ M	k_1K_a sec^{-1}	k_2 $M^{-1}sec^{-1}$	%[a]
25	0.05	1.00×10^{-4}	$.35 \times 10^{-2}$	36.4
25	0.067			29.9
25	0.10			22.2
25	0.20			12.5
25	0.50			5.4
35	0.05	2.77×10^{-4}	$.71 \times 10^{-2}$	43.8
35	0.056			41.3
35	0.067			36.8
35	0.10			28.1
35	0.20			16.3
35	0.50			7.2
45	0.05	6.21×10^{-4}	1.56×10^{-2}	44.3
45	0.067			37.3
45	0.10			28.5
45	0.20			16.6
45	0.50			7.4

(a) Percentage of reaction proceeding by k_1 path calculated by

$$\left(\frac{\frac{k_1K_a}{[H^+]}}{\frac{k_1K_a}{[H^+]} + k_2}\right) \times 100$$

the unprotonated path follows an inner-sphere mechanism since the percentage of ligand released is independent of the $[H^+]$.

As a result of these factors it is proposed here that the reduction of the benzamidopentamminecobalt(III) by Cr(II) is proceeding by parallel reaction paths, that is, both an inner-sphere reaction path, producing $[Cr\text{-}O{=}\overset{NH_2}{\overset{|}{C}}\text{-}C_6H_5]^{3+}$ and $[Cr\text{-}O{=}\overset{NH}{\overset{|}{C}}\text{-}C_6H_5]^{2+}$ complexes and an outer-sphere path, producing $Cr(H_2O)_6^{3+}$. Evidence for parallel reaction paths is seen in the Cr^{2+} reduction of nicotinamidopentaamminecobalt(III) complex.[3] The rates involved for the reduction of the nicotinamide complex are reasonably similar to the rates of the similar reaction of the benzamide complex. To extend the comparison between the nicotinamide complex and the benzamido complex may be dubious as the nicotinamide is bonded through the pyridine nitrogen and inner-sphere attack occurs at the remote C=O of the amide system. In order for parallel reaction paths to be occurring, the rates of reduction of the benzamido complex, by outer- and inner-sphere attack, must be similar.

4-Formylbenzamidopentaamminecobalt(III)

The reduction of the 4-formylbenzamido complex

was found to follow the same rate law as the benzamido complex (III-4).

The rate law is consistent with the reaction scheme

$$(NH_3)_5CoNH_2\overset{O}{\overset{\|}{C}}C_6H_4CHO \overset{K_a}{\rightleftharpoons} (NH_3)_5CoNH\overset{O}{\overset{\|}{C}}C_6H_4CHO + H^+$$

$$(NH_3)_5CoNH\overset{O}{\overset{\|}{C}}C_6H_4CHO + Cr^{2+} \xrightarrow{k_1} \text{products}$$

$$(NH_3)_5CoNH_2\overset{O}{\overset{\|}{C}}C_6H_4CHO + Cr^{2+} \xrightarrow{k_2} \text{products}$$

This mechanism gives the rate law (III-7), if it is assumed that the first step is a rapid equilibrium.

$$\frac{-d(\ln[\text{cobalt(III) complex}])}{dt} = \left(\frac{k_1K_a}{[H^+]} + k_2\right)[Cr^{2+}] \quad \text{(III-7)}$$

The value of K_a has not been determined because of solubility limitations, but is assumed to be less than $[H^+]$ in III-7. Therefore equations (III-4) and (III-7) are identical and $k_1' = k_1K_a$ and $k_2' = k_2$. The values of k_1K_a and k_2 were determined from the slope and intercept of plots of k_{obsd} versus $[H^+]$. Values of k_1K_a, k_2 and activation parameters of the protonated form are summarized in Table 12.

Since K_a could not be measured it is not possible

TABLE 12

Kinetic Parameters for the Reduction of 4-Formylbenzamidopentaamminecobalt(III)

Temp. °C	k_1K_a sec^{-1}	k_2 $M^{-1}sec$	$\Delta H_2^{\ddagger}$ kcal $mole^{-1}$	$\Delta S_2^{\ddagger}$ $mole^{-1}deg^{-1}$
25	1.32×10^{-4}	0.96×10^{-2}	12.7 ± 1.8	-25.3 ± 6.1
35	3.86×10^{-4}	1.99×10^{-2}		
45	1.84×10^{-3}	4.03×10^{-2}		

to calculate the specific rate constant k_1. However it is expected that the K_a of the 4-formylbenzamido complex will be larger than that of the benzamido complex because of the better electron withdrawing ability of the formyl groups. Therefore the K_a of the benzamido complex at 25°C may be used to calculate an upper limit of $k_1 < 6 \times 10^{-3}$ $M^{-1}sec^{-1}$ at 25°C for the reduction of the 4-formylbenzamido complex.

The percentage of ligand transfer was determined spectrophotometrically in a similar manner to that used for the benzamido complex. A slight variation was used, however, in determining the extinction coefficient of the free 4-formylbenzamide ligand as efforts to prepare 4-formylbenzamide failed. The V(II) reduction of the 4-formylbenzamide complex was carried out at $\mu = 1.0$ and $[H^+] = 0.20$ M at 25°, 35°, and 45°C. The V(II) reduction will yield 100% ligand release since all the metal ion products are labile. The observed rate constants for the V(II) reduction are 5.8×10^{-2}, 2.5×10^{-1} and 6.7×10^{-1} $M^{-1}sec^{-1}$ at 25°, 35°, and 45°C respectively. The reduction mixture was ion exchanged and the extinction coefficient of the peak at $\lambda = 249$ nm was determined to be 1.06×10^4 $M^{-1}cm^{-1}$. The electronic

spectrum of the free ligand from the Cr^{2+} reduction solution was the same as that from the V^{2+} reduction. The percentages of the recovered uncoordinated 4-formylbenzamide are given in Table 13. The data indicate that the % transfer is independent of the hydrogen ion concentration, temperature and initial chromium(II) concentration, and that essentially no ligand transfer complex is obtained.

The hydrolysis of the Co(III)-4-formylbenzamido complex shows only a relatively small, if any, acid dependence at 45°C. The observed rate, determined from the average of six runs at varying acid concentrations (0.10 → 1.00 M $[H^+]$), is ~$2.5 \times 10^{-4} sec^{-1}$. Relating these factors to those discussed in the benzamido case, it is seen that very little hydrolysis of the Cr(III) product should occur during the time span of the reduction reactions. In addition it seems reasonable to expect that a carboxamido bound chromium(III) product would have similar hydrolytic stability to that formed with benzamide. Since the latter is detectable it seems reasonable to conclude that an initial carboxamido chromium(III) complex is not destroyed by hydrolysis in the 4-formylbenzamido system.

However, there is the added complication of

TABLE 13

Percent Free 4-Formylbenzamide Recovered after the Reduction Reactions

Temp. °C	$[Cr^{3+}]x10^2$ M	$[H^+]$ M	$[Co^{2+}]x10^3$ M	Percent Free Ligand Recovered
25	5.47	0.05	1.27	100
25	5.60	0.067	1.10	98.1
25	5.47	0.10	1.22	98.9
25	5.60	0.50	1.11	95.2
35	5.41	0.05	1.27	99.2
35	5.47	0.067	1.12	97.6
35	5.47	0.20	1.12	98.5
35	5.47	0.50	1.21	99.0
35	2.74	0.50	1.25	97.7
45	2.71	0.067	1.31	95.4
45	2.71	0.10	1.36	99.4
45	2.71	0.20	1.14	93.0
45	4.06	0.20	1.33	97.7
45	2.73	0.50	1.12	100

Cr^{2+} catalyzed aquation of the initial product. This reaction may take the form of scheme (III-8).

$$Cr^{3+}\text{-O=C(NH}_2\text{)-C}_6\text{H}_4\text{CHO} + Cr^{2+} \xrightarrow[\text{sphere}]{\text{inner}} Cr^{2+} + Cr^{3+}\text{-O=C(H)-C}_6\text{H}_4\text{-C(=O)-NH}_2$$

$$Cr^{3+}\text{-O=C(H)-C}_6\text{H}_4\text{-C(=O)-NH}_2 \xrightarrow{\text{fast}} \text{O=C(NH}_2\text{)-C}_6\text{H}_4\text{CHO} + Cr^{3+} \qquad \text{(III-8)}$$

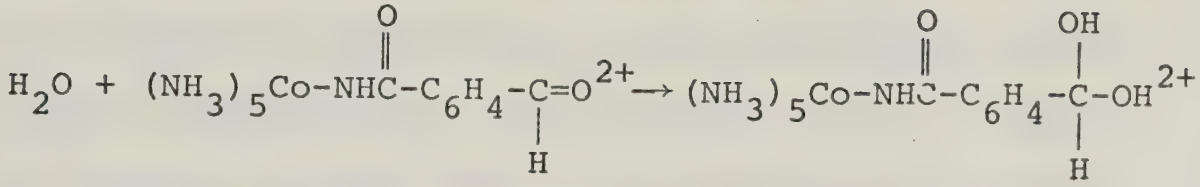
Zanella and Taube[37] have investigated the reduction of p-formylbenzoatopentaamminecobalt(III) and have shown that $Cr^{3+}\text{-O=C(H)-C}_6\text{H}_4\text{CO}_2\text{H}$ is quite labile aquating to form free ligand and $Cr(H_2O)_6^{3+}$. Thus the second step in (III-8) should be fast. It seems unreasonable however that the reduction of the cobalt(III) complex would proceed by adjacent attack and then the Cr(III)-Cr(II) electron transfer proceeds by a remote attack mechanism. Thus inner-sphere adjacent attack is unlikely to be operating.

If an inner-sphere remote attack were occurring in the reduction of the cobalt(III) complex then $Cr^{3+}\text{-O=C(H)-C}_6\text{H}_4\text{-C(=O)-NH}_2$ would be formed. Again, this product is probably quite labile and aquation will be fairly rapid. Therefore this is consistent with the product analysis. It is unlikely, however, that an inner-sphere remote attack mechanism is operating because of the rate similarity to the reduction of

the benzamido complex as is discussed later.

The 4-formylbenzamido system may be further complicated by hydration of the aldehyde group. Inner-sphere remote attack might be hindered by the hydration of the aldehyde group under acidic conditions. Subsequent to the completion of most of the experimental work here evidence for this effect in the 4-formylbenzonitrile system was received.[30] The hydration of the aldehyde is thought to be slow in neutral solution but quite fast in acid. As a test for this idea kinetic runs parallel to the earlier ones were performed in which Cr^{2+} is added to the complex in neutral solution (H^+ added a short time (< 30 sec) before Cr^{2+} added) while in earlier runs the Cr^{2+} was added to complex in acidic solution (solution of Co(III), $LiClO_4$ and $HClO_4$ degassed for ~ 20 minutes then Cr^{2+} added). At the three acid concentrations studied ($[H^+]$ = 0.50, 0.10, 0.067 M) there seems to be a general 3-fold increase in rate of reductions of the solution prepared by the former method. There may be some error because of the small absorbance change, but the increase is not expected to be completely explainable by this. It is probable then that either the hydrate, as described in scheme (III-9) or an equilibrium

mixture is being reduced.



(III-9)

However the factor of only three-fold difference in rates indicates that neither form is being reduced much faster than the other. A similar scheme to (III-9) was postulated for the pentaammineruthenium-(III) complex of 4-formylpyridine.[38] If the p-formyl group is hydrated under the reaction conditions in this study then $(NH_3)_5CoNHC(=O)-C_6H_4-C(OH)H-OH^{2+}$ and $(NH_3)_5CoNH_2C(=O)C_6H_4C(OH)H-OH^{3+}$ predominate. If there is a large degree of hydration of the ligand, inner-sphere remote attack is unlikely because, although the remote oxygen has two pairs of electrons, conjugation of oxygen to the benzene ring is not possible because the carbon atom is saturated in the hydrate form.

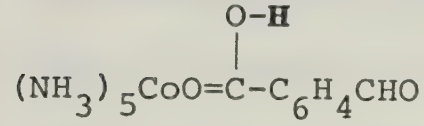
Because of the inability to rule out Cr^{2+} remote attack without the use of rate comparisons and because of the possibility of hydration of the aldehyde oxygen, the products of the reaction are not necessarily definitive of the reaction mechanism.

Since the product analysis is not helpful in ascertaining the reduction mechanism, relative rate

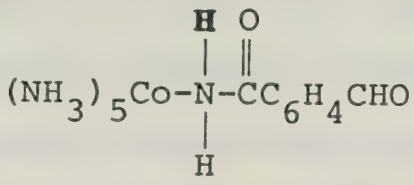
arguments may provide some guidelines. It must first be noted that although the 4-formylbenzamido system may be complicated by some hydration of the aldehyde it seems that both forms of the complex are reduced at similar rates. Evidence for an outer-sphere reduction of the 4-formylbenzamido complex is afforded by a comparison with the 4-formylbenzoatopenta-amminecobalt(III) (PFB). The reduction of PFB has been shown to proceed with formation of $[(H_2O)_5CrO{=}CHC_6H_4CO_2H]^{2+}$ and therefore follows an inner-sphere remote attack mechanism. The rate of reduction of PFB by Cr^{2+} is ~5 x 10^5 faster than that of the 4-formylbenzamido complex. The large rate difference seems to clearly indicate a different mechanism for the latter and the logical conclusion would be that it is following an outer-sphere mechanism since it has already been argued that adjacent attack is unlikely with the 4-formylbenzamido complex.

It might also be noted that the $[H^+]$ term in the rate law for reduction of PFB with k = 3.8 x 10^2 $M^{-1}sec^{-1}$, should be analogous to reduction of the protonated form of the amide, but this does not seem to hold. The lack of any parallel between the two complexes is consistent with Taube's argument that, for the carboxylate system, the proton goes

onto the adjacent carbonyl oxygen as in (3), thereby improving the reducibility of the ligand and the conjugation with the remote group.



(3)



(4)

But in the amide ligand (4) if the proton goes on the nitrogen then it has the effect of hindering conjugation between the remote group and the cobalt(III) center, although it may improve the reducibility of the ligand.

The similarity in the rates of reductions of benzamido- and 4-formylbenzamido cobalt(III) complexes by Cr^{2+} suggests that they are both following the same mechanism. If the 4-formylbenzamido cobalt(III) complex was being reduced by an inner-sphere remote attack mechanism, it is felt that its rate would be much faster than the rate of reduction of the benzamido complex. Evidence for this is the fact that PFB is reduced 350 times faster than the benzoato complex , the former by remote attack and the latter by adjacent attack.

The activation parameters shown in Table 12

agree with the general rule noted in the discussion of the benzamido complex for an outer-sphere mechanism. The study on the rate of reduction of the formamidopentaamminecobalt(III)[1] indicated that all protonated forms of N-bonded carboxamido complexes should follow an outer-sphere reaction mechanism because of lack of conjugation through to cobalt(III).

An outer-sphere mechanism is then reasonable for the protonated form of the 4-formylbenzamido complex. A question arises, however, as to why the unprotonated form does not proceed by remote attack analogous to PFB. The only explanation that can be offered at the moment is that the $-CONH^-$ group does not increase the reducibility of the ligand as much as $-CO_2^-$ group. The reducibility effect of these two groups may be a normal substituent effect, for example the $-CO_2^-$ group may have a greater electron withdrawing effect than the $-CONH^-$ group. The effect also could be due to the difference in the ability of these two groups to transfer the inductive effect of the $(NH_3)_5Co^{3+}$ to the organic ligand.

At this point in our discussion it is appropriate to discuss the intimate mechanisms of Cr^{2+} reduction of the benzamido- and 4-formylbenzamido complexes. Both complexes are most likely to have major outer-

sphere pathways. Either a simple outer-sphere or an outer-sphere radical ion or superexchange mechanism[6] must be applicable. In the simple outer-sphere case the electron is transferred from the reductant directly into the oxidant orbital, however, in the radical ion or superexchange mechanism the electron is transferred from the reductant directly into a ligand orbital without bridge formation. The reducibility of the ligand for the latter mechanisms is important.[6,36] In comparing the Hammett σ^- value for -CHO substituent group (1.10)[39] to the -H substituent group (0.00) it can be seen that the CHO group should greatly increase the reducibility of the ligand. This suggests that the rate of reduction of the 4-formylbenzamido cobalt(III) complex by Cr^{2+} should be much faster than the benzamido complex. However, experimental results show these rates to be similar. As a result the major pathway for the Cr^{2+} reduction of both complexes in this study are thought to be proceeding by a simple outer-sphere and not an outer-sphere radical ion mechanism.

To explain the ~11% ligand transfer product observed for the benzamido complex a minor inner-sphere pathway was proposed. Inner-sphere reductions are known to occur by three major paths: adjacent

attack, adjacent attack with chelation, and remote attack. Adjacent attack with chelation (complex must have two potential donor atoms) and remote attack (complex with ligands having a conjugated bond system from a remote polar group to the coordinated atom) are not possible for the benzamido complex. As a result the minor pathway for Cr^{2+} reduction of the benzamidopentaamminecobalt(III) complex must be proceeding by an inner-sphere adjacent attack mechanism. No ligand transfer product is observed for the 4-formylbenzamido complex. It has been argued previously that inner-sphere adjacent attack could not explain the product analysis for the 4-formylbenzamido system. The adjacent attack mechanism in this system could have a similar rate to that in the benzamido but it is not observed because the outer-sphere path is now ~ 3 times faster than with benzamido.

CHAPTER IV

CONCLUSIONS

In principle the carboxamide group can show linkage isomerism since it may coordinate through the carbonyl oxygen or the amide nitrogen. Protonation studies of uncomplexed amides strongly favor oxygen as being the most basic group under strongly acidic conditions. As a result it is normal to expect the oxygen bonded isomer of carboxamido metal complexes to be most easily prepared, as is the case for the formamido[1] and several other $(NH_3)_5Co^{3+}$ complexes noted in Gould's work.[8] The base hydrolysis of coordinated nitriles has been used in this study to prepare the N-bonded carboxamido cobalt(III) complexes. The results of this plus Sargeson's[40] work indicate that this is a clean and rapid method of preparing both aliphatic and aromatic carboxamide complexes.

The chemistry of the N-bonded carboxamide group, for two aromatic carboxamides, has been studied in this work. The $(NH_3)_5Co^{3+}$ nitrogen bonded amides are hydrolytically stable in aqueous acid ($t_{1/2}$ ~ 3000 sec at 45°C). Benzamidopentaammine-cobalt(III) is a moderately strong acid having a

pK_a = 1.65 at 25°C. A general acid strengthening effect by $(NH_3)_5Co^{3+}$ of > 10 pK_a units can be seen on comparing the free ligands to their coordinated N-bonded counterparts. This change can be understood in terms of the electron-withdrawing effect of the pentaamminecobalt(III) unit.

Coordination to $(NH_3)_5Co^{3+}$ has had the effect of increasing the rate of hydrolysis of nitriles to their respective amides. In general a rate enhancement in the range of ~ 10^6 seems to occur in the alkaline hydrolysis of a nitrile when it is coordinated to $(NH_3)_5Co^{3+}$. Apparently the electron withdrawing power of $(NH_3)_5Co^{3+}$ increases the susceptibility of the nitrile carbon atom to attack by a nucleophile. Rate enhancement of nitrile hydrolysis by metal ions seems to be a general effect since it was previously found by Breslow *et al*[14] that the rate of hydrolysis of 2-cyano-1,10-phenanthroline is enhanced 10^7 times in the presence of Ni^{2+} and 10^9 in the presence of Cu^{2+}. M. A. Bennett and T. Yoshida[15] recently have presented a preliminary report on the hydration of simple aliphatic nitriles to the corresponding carboxamides catalyzed by Pt(II) hydroxy complexes. This system is not well characterized, but the authors proposed that the

reaction involves insertion of the nitrile into the Pt-OH bond followed by rapid rearrangement to the N-amido complex; this hydrolyzes to yield the free amide.

From the present work it is apparent that aromatic amide complexes of $(NH_3)_5Co^{3+}$ are reduced by Cr^{2+} mainly by an outer-sphere mechanism. This is considered surprising for the 4-formylbenzamido complex. The formyl substituted ligand was expected to be easily reduced, by an inner-sphere remote attack mechanism, based on a comparison of the rates of reduction and product analysis from the p-formylbenzoato and benzoato complexes. One can only conclude that the carboxamide group decreases the reducibility of the ligand so that the outer-sphere mechanism is favored over inner-sphere remote attack. A minor inner-sphere adjacent attack path was noted for the benzamido complex. A comparison to its analogue, benzoatopentaamminecobalt(III) complex, indicates that adjacent attack is much less favored for the N-bonded carboxamides than for the carboxylates.

In consequence of the work done on the benzamido and 4-formylbenzamido cobalt(III) complexes, it seems necessary to find a group better suited for remote attack than the formyl group if a radical ion inter-

mediate is to be found for the Cr^{2+} reduction of a carboxamide cobalt(III) complex. Unfortunately this may not be feasible if a substituent with a larger σ^- value[39] than that of -CHO is necessary to improve the reducibility. A possible application of the nitrile hydrolysis reaction would be in the preparation of organic amides where the mild conditions would be advantageous. The carboxamide complex could be destroyed by hydrolysis or reduction and the free ligand recovered. This method has a serious drawback however in that the nitrile complexes can only be made in low yield as yet. For the moment the more labile Pt(II) system studied by Bennett and Yoshida seems to hold more promise for the facile conversion of nitriles to amides.

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